SPAWAR Validates Sampler for Underwater Detection of Munitions Constituents

Polar Organic Chemical Integrative Samplers Deemed More Effective Than Other Methods

A RESEARCH EFFORT led by Gunther Rosen of the Space and Naval Warfare Systems Command, Systems Center Pacific (SSC Pacific), and funded by the Navy Environmental Sustainability Development to Integration (NESDI) program and Environmental Security Technology Certification Program (ESTCP), demonstrated that a new kind of passive sampler has the potential to provide the first truly definitive answers with regard to the presence of munition constituents in the marine environment.

Navy's firing ranges are, or were, located near coastal environments, there is concern regarding their potential for blast-related risks to humans or ecological damage to the environment. Discarded military munitions (DMM), which have been purposefully and improperly disposed of in underwater environments, present similar concerns.

Underwater munitions may pose a risk to the marine environment if the unexploded weapon becomes corroded or breaches, which may cause the explosive fill material to leak or dissolve into the surrounding environment. UXO or DMM may contain munitions constituents (MC) such as 2,4,6-trinitrotoluene (TNT) and hexahydro-1,3,5-trinitro-1,3,5-triazine (RDX), which are among the most widely-used high explosives.

Although the Navy and others have recently developed an improved understanding of the environmental fate and effects of MC that could leak from underwater munitions through extensive laboratory experimentation, there are still questions about what constitutes environmentally relevant concentrations of munition constituents.

Identifying leaking underwater munitions and measuring MC at low concentrations is highly challenging, in part because introduction of the constituents to the water column may be episodic in nature and grab sampling is unlikely to accurately characterize water concentrations over time. (Note: "Grab sampling" is the common phrase used to describe the collection of a water sample into a bottle at a distinct moment of time).

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Underwater Munitions

Unexploded ordnance (UXO) are explosive weapons (including bombs, projectiles, and mines) that did not explode when they were employed, and therefore, still pose a risk of detonation, in many cases, decades after they were fired during live-fire training or testing. Because many of the

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This project was formed to identify a cost-effective, field deployable sampling method that features detection at ultra-low concentrations, and provides time-weighted average concentrations (i.e., average estimated water concentrations over deployments of two weeks or more) for improved characterization of MC at underwater UXO sites.

Example of Composition B.

Personnel from SSC Pacific and the U.S. Army Engineer Research and Development Center, with assistance from Oklahoma State University, optimized the use of a commercially available Polar Organic Chemical Integrative Sampler (POCIS) for the detection of MC in aquatic environments. The POCIS is a high-sorption sampler widely used to detect polar contaminants including pesticides, pharmaceuticals and household products.

Phase 1 of the project involved laboratory testing of two types of POCIS samplers. Both sampler types, one originally developed for detection of pharmaceuticals and one for pesticides, were placed in 10-gallon aquarium tanks. Both were able to detect and quantify small quantities of RDX and TNT dissolved from the common explosive formulation Composition B (a combination of TNT and RDX), even at high levels of water replacement (five turnovers per day) and when the Composition B was partially encased, minimizing contact with surrounding water.

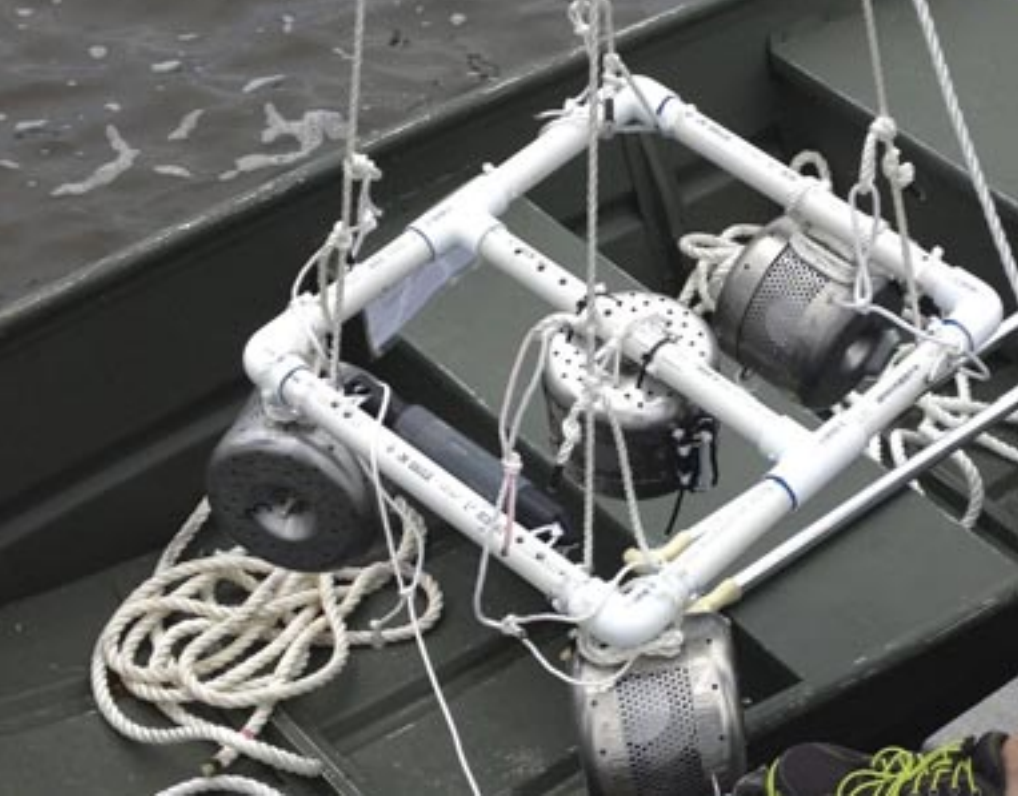
About POCIS

POCIS simplifies the sampling process by eliminating the time and effort involved to conduct multiple grab sampling events and multiple analyses. The ability to deliver time-weighted average (TWA) concentrations means that the POCIS will record intermittent emissions that may otherwise be missed by scheduled grab sampling events. The POCIS is also more sensitive, recording chemicals at ultra-low levels, and preserves the contaminants of concern once they come into contact with the sorbent. Traditionally-collected water samples can degrade during storage and transport from the field to the laboratory. POCIS sampling also eliminates the electrical or fuel powering requirements associated with other types of sample preparation.

Enabling the Field Demonstration

COOPERATION BETWEEN MULTIPLE entities was required to make the POCIS demonstration a success. The following permissions, permits or documents were required before work could commence.

- The Florida Department of Environmental Protection. This agency granted authorization to use State submerged lands without obtaining a regulatory permit.
- U.S. Army Corps of Engineers (USACE) Nationwide Permit 5. The Corps evaluates permit applications for essentially all construction activities that occur in the nation's waters, including wetlands.
- Technical fact sheets for TNT and other chemicals were reviewed and utilized. Review of the USACE Engineer Research and Development Center Health and Safety plan for environmental research conducted with high explosives.
- EPA's Gulf Ecology Division. Coordination with the safety and health manager.



Fragments of Composition B were added to metal canisters with mesh-like sides and suspended from a research dock just above the sea floor.

The Toxicity Issue

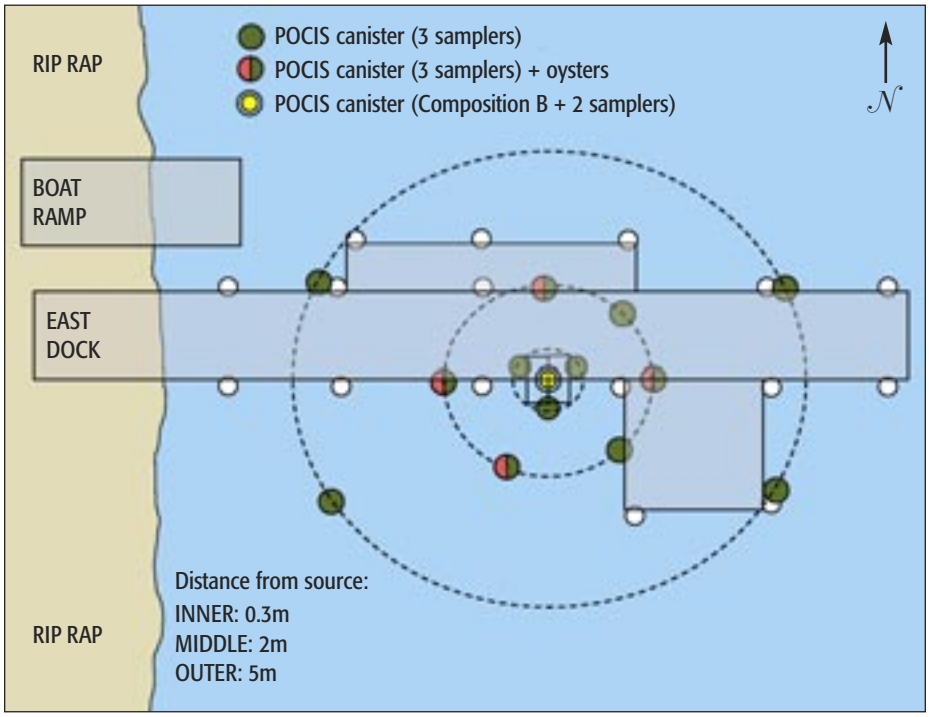
A previous NESDI project (project no. 258) focused on the development of toxicity and bioaccumulation benchmarks for common MC, including TNT, RDX, and their degradation products. The project results suggested low ecological risk under expected exposure scenarios in the marine environment. This conclusion is substantiated by the development of a large body of data illustrating that these chemicals typically undergo extensive degradation processes upon contact with marine sediment, and that relatively high concentrations of these chemicals would be required to produce toxic effects. Additionally, these chemicals have virtually no potential for trophic transfer from invertebrates to fish, and thus, very low likelihood of exposure to humans via the food chain. The minimal potential for toxicity under realistic exposure conditions is also related to the very low propensity for these chemicals to bioaccumulate. NESDI-funded toxicity and bioaccumulation studies have consistently exhibited similar results relating to low toxicity and bioaccumulation using a variety of species, including benthic (bottom-dwelling) and pelagic (deep sea) invertebrates and fish.

Laboratory-based experiments show that MC presence, at concentrations of concern in aquatic environments, are expected to be localized (i.e., adjacent to leaking shells), episodic (very slow and intermittent), and influenced by the level of projectile corrosion and site conditions (e.g., temperature, currents).

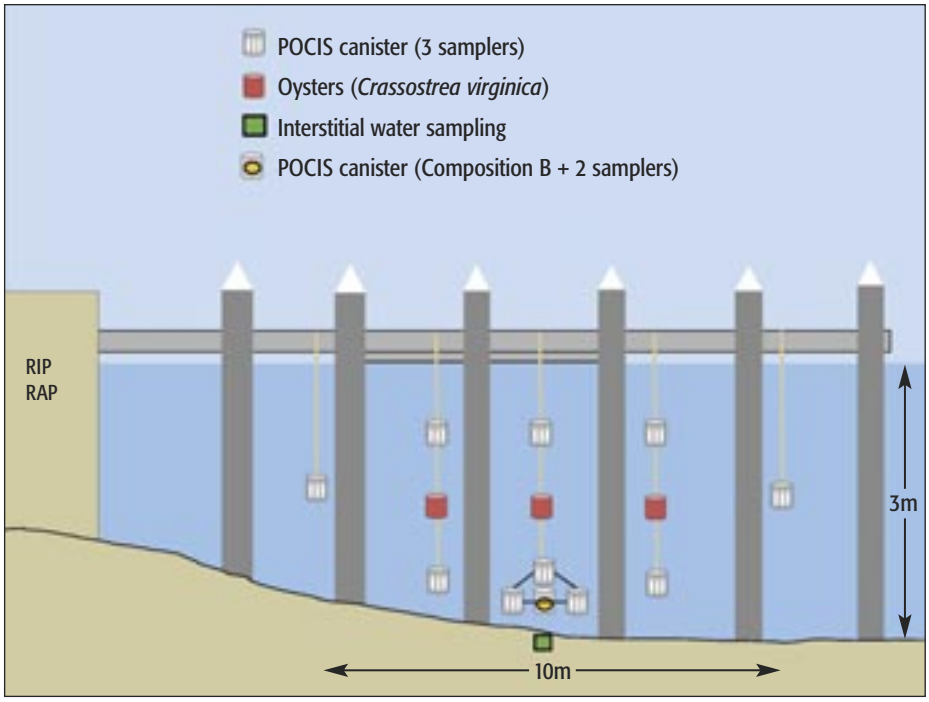
The laboratory tests conducted by this project team confirmed that method detection limits for POCIS were expected to be under 50 nanograms per liter for most compounds—well below levels associated with biological impacts.

The Field Demonstration

A field demonstration of the POCIS was conducted in 2014 adjacent to the U.S. Environmental Protection



A concentric circle sampling design was employed to examine uptake by the POCIS at increasing distances from the source.



Schematic of canister placement.

Agency's (EPA) Gulf Ecology Division at Santa Rosa Sound, Florida. This site, near Pensacola Bay, was chosen because it exhibits some of the same physical characteristics as many sites where Department of Defense (DoD) training ranges exist (i.e., sandy sediment, brackish water, and subtropical temperatures), and was previously established as not having any MC in a preliminary study.

Fragments of Composition B were added to metal canisters with mesh-like sides and suspended from a research dock just above the sea floor. This configuration roughly simulated exposure of explosive fill material inside a breached munition, providing a point source for potential exposure to the water column. For each of the 20 sampling locations, three POCIS samplers were placed inside identical canisters and deployed at varying distances, directions, and depths, from the "source" canister containing Composition B. The source canister also contained two POCIS samplers for measuring MC concentration inside the canister. A concentric circle sampling design was employed to examine uptake by the POCIS at increasing distances from the source.

Because bivalves have often been used as natural "samplers" for the detection of contaminants, oysters were also deployed. Concurrent grab water and sediment sampling was also conducted.

After 13 days, all samplers were removed and sent to Dr. Jason Belden at an environmental toxicology laboratory at Oklahoma State University for analysis. The highest concentrations of TNT and RDX (the most common constituents measured), based on POCIS-derived average water concentration, occurred within 0.3 meters from the source, with rapid reduction to non-detectable levels only several meters away. However, all POCIS-derived water concentrations were several orders of magnitude lower than those required to be toxic.

The POCIS sampler alongside a more traditional sampling method, oysters.

Boat deployment to visit the next POCIS demonstration site at Bahia Salina del Sur, Vieques, Puerto Rico.

The tissue, grab water samples and sediment samples returned non-detectible concentrations for all constituents, confirming that the POCIS is the more sensitive instrument, with lower limits of detection.

A second 32-day deployment was conducted on a smaller scale. The TWA water concentrations for all constituents showed the same trends of lower MC concentration with increasing distance from the source, but were substantially lower than the 13-day averages. The reasons for this difference are still under investigation and could be due to a variety of environmental factors, including biofouling, which may have affected Composition B dissolution and uptake by the samplers.

What's Next

The next phase of this effort, sponsored by ESTCP, will be implementation of the POCIS at Vieques, a former naval training range in Puerto Rico. From the mid-1940s until 2003, more than 300,000 munitions items were fired during military training operations on and around this island, including naval gunfire, air-to-ground bombing, and marine artillery fire. So far, approximately 40,000 munitions items have been recovered, but it is estimated that up to 9,000 acres of the property may contain munitions and munitions-related items. Many of these items are likely "dummy" bombs or even pieces of debris. Placement of POCIS samplers in the area will provide critical information as to whether or not these items are actively contributing MC into the underwater environment, and help determine whether removal is warranted. This demonstration is scheduled to commence in late 2015.

The Bottom Line

For decades, the absence of definitive sampling and analysis techniques have subjected former military training and bombing ranges to high uncertainty, and potentially unnecessary and overly conservative assumptions of

The Basics About ESTCP

ESTCP IS DOD'S environmental technology demonstration and validation program. The program was established in 1995 to promote the transfer of innovative technologies that have successfully established proof of concept to field or production use. ESTCP demonstrations collect cost and performance data to overcome the barriers to employ an innovative technology because of concerns regarding technical or programmatic risk.

The program's goal is to identify and demonstrate the most promising innovative and cost-effective technologies and methods that address DoD's high-priority environmental requirements. Formal demonstrations are conducted at DoD facilities and sites in operational settings to generate full documentation towards the goals of full field validation, improved performance and cost savings. To ensure the demonstrated technologies have a real impact, ESTCP engages with end users and regulators throughout the development and execution of each demonstration. Transition challenges are overcome with rigorous and well-documented demonstrations that provide the information needed by all stakeholders for acceptance of the technology.

For more information, visit the program's web site at www.serdp-estcp.org.

Examples of munitions debris in near-shore environments.
U.S. Army Corps of Engineers

The Basics About the NESDI Program

THE NESDI PROGRAM seeks to provide solutions by demonstrating, validating and integrating innovative technologies, processes, materials, and filling knowledge gaps to minimize operational environmental risks, constraints and costs while ensuring Fleet readiness. The program accomplishes this mission through the evaluation of cost-effective technologies, processes, materials and knowledge that enhance environmental readiness of naval shore activities and ensure they can be integrated into weapons system acquisition programs.

The NESDI program is the Navy's environmental shoreside (6.4) research, development, test and evaluation program. The program is sponsored by the Chief of Naval Operations Energy and Environmental Readiness Division and managed by the Naval Facilities Engineering Command out of the Naval Facilities Engineering and Expeditionary Warfare Center in Port Hueneme, California. The program is the Navy's complement to ESTCP which conducts demonstration and validation of technologies most relevant to the tri-Services, EPA and Department of Energy.

For more information, visit the NESDI program web site at www.nesdi.navy.mil or contact Ken Kaempffe, the NESDI Program Manager at 805-982-4893, DSN: 551-4893 or n.kaempffe@navy.mil.

ecological risk. POCIS is the first continuous sampling technology that records ultra-low levels of constituents of concern at low cost with more accuracy than any previous system. It is expected that their use will contribute towards environmental evaluations of risk, and assist with cleanup decisions, while easing concerns of both regulators and the general public.

The final report containing the results of laboratory work, the field work conducted in Santa Rosa Sound, and user guidelines is expected to be complete by press time. For a copy, contact the Principal Investigator (below) or search for "project 465" on the NESDI web site at www.nesdi.navy.mil (username and password required). ⚓

Gunther Rosen
Space and Naval Warfare Systems Command, Systems Center Pacific
619-553-0886
DSN: 553-0886
gunther.rosen@navy.mil